A Selective Joint Determination of Salicylic Acid in *Actinidia chinensis* Combining a Molecularly Imprinted Monolithic Column and a Graphene Oxide Modified Electrode

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A new combination between selective polymer monolith microextraction (PMME) and sensitive differential pulse voltammetry (DPV) was developed for the determination of the phytohormone salicylic acid (SA) in *Actinidia chinensis*. A molecularly imprinted monolithic column (MIMC) thermally *in-situ* polymerized in a micropipette tip by using SA as a template, 4-vinyl pyridine (4-VP) as a functional monomer and ethylene glycol dimethacrylate (EGDMA) as a cross-linker in the mixed porogen of toluene and dodecanol, was employed for the microextraction of SA. The prepared MIMC was characterized by a Fourier transform infrared spectrometer (FT-IR), scanning electron microscope (SEM) and thermo gravimetric analysis (TGA). The results confirmed the binary continuous structure of the porous network. The extracted SA was determined by DPV on a graphene oxide (GO) modified electrode. The joint conditions between MIMC and DPV were investigated practically. Under the optimum conditions, SA could be determined selectively and sensitively in a linear range from 0.1 to 60.0 μg g⁻¹. The limit of detection was 0.03 μg g⁻¹ and the recoveries were between 86.2 and 105.2%. The proposed joint method was successfully used to determine SA in *Actinidia chinensis*.

Keywords Salicylic acid, molecularly imprinted monolithic column, polymer monolith microextraction, graphene oxide, *Actinidia chinensis*

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Introduction

Phytohormones are a collection of naturally engendered molecules that play key roles in regulating physiological processes in plants at low concentration. They could affect numerous aspects of plant growth and development, including cell proliferation and differentiation, seed germination, organ formation, stem elongation, senescence, etc. Salicylic acid (SA) is one of the phytohormones that possess an aromatic ring with a hydroxyl group and a carboxyl group (Fig. 1). Usually, SA acts as an essential signaling molecule, having diverse effects on the tolerance to both biotic as well as abiotic stresses in plants; these include drought, flood, wounding, undernourishment, or insect and pathogen attack, etc.

Many electroanalytical methods have been applied to the quantitative determination of SA in real samples owing to its advantages of simplicity, convenience and low cost over other analytical methods. Though electrochemistry is sensitive and convenient for the determinations of many molecules, the selective analysis of SA in various matrices is still a difficult task because of the complex interfering components and its trace concentration in the matrixes, which to some extent complicate and overburden the subsequent preparation of modified electrodes, and also limit the application of electroanalysis in real samples due to poor selectivity.

In order to enhance the selectivity of electroanalysis for SA and to simplify the establishment of modified electrodes, we considered introducing some pretreatment methods into the electroanalysis of SA in real samples. There are diverse pretreatment procedures. Wu et al. determined SA and three other acidic phytohormones in natural coconut juice using hollow fiber-based liquid-liquid-liquid microextraction (HF-LLLME) as a sample pretreatment. Bai et al. reported a single-drop liquid-liquid-liquid microextraction (SD-LLLME) to determine SA in fruit juice. Aresta et al. employed solid-phase microextraction (SPME) with a polydimethylsiloxane-divinylbenzene fiber to simultaneously detect SA and its derivatives in selected fruit, vegetables and beverages. Wang et al. developed a new method of ion-pair stir bar sorptive extraction (IP-SBSE) to determine three acidic phytohormones including SA in cucumbers and green bean sprouts, etc. Among them, polymer monolith-microextraction (PMME) based on a molecularly imprinted polymer (MIP) drew our attention owing to its simplicity, selectivity and versatility.

PMME is one kind of SPME that uses a polymer monolith as the sorbent, while the MIP technology is achieved by copolymerizing functional monomers and cross-linkers in the...
presence of a template. Once the template is removed, complementary microcavities are obtained that allow rebinding of the template or some structurally related compounds. Traditionally, the MIPs of SA or other hydroxybenzoic acids are mainly prepared by bulk polymerization that needs to be crushed, grounded, sieved and packed.\(^{[19,20]}\) Or surface imprinting, which creates more affinity sites on the surface of the supports.\(^{[21]}\) To the best of our knowledge, the MIP monolithic column of SA using \textit{in situ} synthesis, which greatly simplifies the preparation has not yet been reported, as well as a combination between PMME and electroanalysis of SA in plant samples. However, new problems are associated with this combination. Firstly, the organic solvent in an eluent derived from the process of PMME may have an effect on the electroanalysis of SA; secondly, the used buffer solutions in the electroanalysis may change the volume of the eluent, and thus influence the effect of enrichment. Thus, the present aim is to circumvent these analytical problems and develop a valid and novel method for the determination of SA in plants.

Here, a molecularly imprinted monolithic column (MIMC) was synthesized in a micropipette tip by \textit{in situ} thermal initiated polymerization using SA as a template, 4-vinyl pyridine (4-VP) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross-linker, toluene–dodecanol as binary porogenic solvents and 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The micropipette tip could match to a syringe without any other treatment to perform the PMME. The determination of SA was performed by differential pulse voltammetry (DPV) on a graphene oxide (GO) modified glassy carbon electrode (GCE), due to the advantages of GO, such as a nano-scale effect, the surface properties, easy handling and strong affinity with biological molecules.\(^{[22]}\) The conditions of microextraction and electroanalysis were optimized, especially the joint condition between PMME and DPV. Thus, a new method for the detection of SA in \textit{Actinidia chinensis} using the MIMC-DPV was successfully established.

\section*{Experimental}

\subsection*{Reagents and chemicals}
All chemicals were of analytical reagent grade. Water was of HPLC-grade, generated by an Ultrapure Water System (Beijing, China). Acetonitrile (ACN) and methanol (HPLC grade) were obtained from Tedia (Ohio, USA). Salicylic acid (SA), 4-vinyl pyridine (4-VP), ethylene glycol dimethacrylate (EGDMA), dodecanol and toluene were obtained from Aladdin (Shanghai, China). 2,2′-Azobisisobutyronitrile (AIBN) was procured from Kermel Chemical Reagents Development Center (Tianjin, China). Graphene oxide (GO) was purchased from XF NANO (Nanjing, China).

Stock standard solutions of SA (1 mg mL\(^{-1}\)) were prepared in methanol and stored in the dark at 4°C. Working solutions were made by the dilution of a SA stock solution with ultrapure water. A phosphate buffered solution (PBS) was used as a supporting electrolyte. The pH of the buffer could be regulated by the addition of either 0.1 mol L\(^{-1}\) HCl or 0.1 mol L\(^{-1}\) NaOH.

\subsection*{Synthesis of MIMC}
A synthetic schematic of MIMC is displayed in Fig. 1. SA (13.8 mg) and 4-VP (43.0 µL) were dissolved in a 0.92-mL mixture of toluene and dodecanol (5:18, v/v) and sonicated for 2 h at room temperature to perform pre-polymerization. Then, EGDMA (305 µL) and AIBN (16 mg) were added to the mixture and sonicated to form a homogeneous solution. The mixture was deaerated with nitrogen for 5 min and then transferred into micro pipette tips at a volume of 100 µL. The micro pipette tips had been sealed at one end in advance, and the other end was sealed with a homemade cap after the tips had been filled with the pre-polymerization mixture. Then, the polymerization was thermally initiated at 60°C in an oven for 24 h. After polymerization, the monolithic column was washed with methanol to remove the template molecule. As a reference, a non-imprinted monolithic column (NIMC) was prepared analogously, as described for the MIMC, but without a template.\(^{[23]}\)

\subsection*{Fabrication of GO-GCE}
A bare GCE of 3 mm diameter was polished with an aqueous alumina (0.05 µm) slurry on a wet polishing cloth, and then rinsed with ultrapure water and sonically cleaned in a HNO\(_3\)-water mixture (1:1, v/v), ethanol and ultrapure water for 5 min, respectively, to remove any trace of alumina. GO powder (5 mg) was added to ultrapure water (2.5 mL) and sonicated for 30 min. The well-polished GCE was modified by dropping 10 µL of the homogenized GO dispersion over the electrode surface, followed by drying under an infrared lamp for 30 min.

\subsection*{Sample preparation}
\textit{Actinidia chinensis} was purchased from a local market in Wuhan, China. Fruits of uniform size and without visible physical injuries were selected. Prior to extraction, the peeled \textit{Actinidia chinensis} material was cut into small pieces and homogenized by grinding with a mortar and pestle. Then, 1.0 g of the homogenized sample was immersed in a 10.0-mL mixture of methanol–water-acetic acid (10:89:1, v/v/v) for 16 h at 4°C in the dark to perform extraction.\(^{[24]}\) After 10 min of centrifugation at 4000 rpm, the supernatant was filtered through a 0.22-µm membrane (Xingya Scavenging Material Company, Shanghai, China). Then, the filtrate was rotary evaporated to yield a
residue that was subsequently reconstituted in 250 mL ultrapure water and stored at 4°C prior to analysis.

**PMME procedures**

An LSP01-1B longer pump (Baoding Longer Precision Pump Co. Ltd., China) was utilized to perform the PMME. Before sample loading, the synthesized monolithic column was conditioned with 1 mL of methanol, followed by 0.3 mL of water for equilibration. Then, 5.0 mL of the pretreated sample solution was loaded through the MIMC at a flow rate of 0.2 mL min⁻¹ and then washed with 0.3 mL of water. The retained analytes were eluted with a 0.5-mL mixture of PBS (1 × 10⁻³ mol L⁻¹, pH 3.0)–ACN (4:6, v/v) at a flow rate of 0.05 mL min⁻¹. The eluent was diluted to 1.5 mL with the addition of PBS (1.0 × 10⁻³ mol L⁻¹, pH 3.0) for further electrochemical analysis.

**Voltammetric determination of SA in plant extract**

After PMME, as shown in Fig. 1, SA was determined in the diluted eluent by DPV using the prepared GO-GCE. The DPV runs were recorded in a potential range varied from +1.6 to +0.6 V, at a scan rate of 40 mV s⁻¹, a pulse amplitude 50 mV, a sample width 20 ms, a pulse width 50 ms, a pulse period of 500 ms, and a sensitivity 1 × 10⁻⁵ A V⁻¹. The height of the peak was analyzed and the amount of SA was determined by a method of standard aliquot addition. All of the electrochemical tests were carried out in a single three-electrode cell with a Pt wire and an aqueous saturated calomel electrode (SCE).

**Results and Discussion**

**Synthesis mechanism of MIMC**

We firstly synthesized the SA imprinted monolithic column by in situ polymerization in micro pipette tips, which has several merits, such as less consumption of the solvents, a high extraction efficiency and simplicity of preparation compared with bulk polymerization and surface imprinting.²⁴,²⁵ A synthetic schematic of MIMC is shown in Fig. 1. The copolymerization of 4-VP (as the mono-functional monomer) and EGDMA (as the cross-linker) may produce a poly (4-VP-co-EGDMA) macroscopic network by free-radical polymerization.²⁵ The physical properties of the polymer-like pore size and the surface area are usually influenced by tailoring of the prepared conditions, such as the type and percentage of the functional monomer, cross-linker and porogen. Since SA is a diprotic acid, 4-VP was chosen as the functional monomer to form electrostatic interactions with SA, and the optimal molar ratio of SA and 4-VP was 1:4, according to the literature.²⁴,²⁵ Besides, the volume of EGDMA was optimized and the best molar ratio of SA, 4-VP and EGDMA was 1:4:16 (Fig. 2b), which was more homogeneous in appearance, and allowed the synthesized...
polymer to display a suitable flow rate and a lower back pressure in the PMME process.

Characterization of MIMC

The morphology of the prepared MIMC was investigated by SEM (X-650, Hitachi, Japan), and is illustrated in Fig. 2a. The monolithic column was observed to possess binary continuous structures: network skeleton and macropores, which ensure fast mass transfer and low back pressure in the microextraction process.

FT-IR (PerkinElmer, USA) spectra of EGDMA, MIMC and NIMC are presented in Fig. 3a. EGDMA shows characteristic peaks at 1718 cm⁻¹ of C=O stretching vibration and 1637 cm⁻¹ of C=C vibration, respectively. Compared with EGDMA, there are stronger C=O stretching vibrations at 1729 cm⁻¹ and weaker C=C stretching vibration at 1637 cm⁻¹ in the infrared spectrogram of MIMC and NIMC, which indicates that EGDMA has been successfully cross-linked among the polymers monolith.

TGA (TGA-7, PerkinElmer, USA) was utilized to evaluate the stability of MIMC. As shown in Fig. 3b, the weight of the MIMC decreased twice when the temperature increased to nearly 150 and 300°C, due to the decomposition of 4-VP and EGDMA respectively. This indicates that the MIMC is stabilized at nearly 150°C, which reveals that the material has a high thermal stability.

Chromatographic analysis of SA

The chromatograms of SA and other phytohormones in the eluent after PMME with MIMC or NIMC are shown in Fig. 3c. The chromatographic analysis was performed on a HPLC system with a UV detector (Dionex Summit U3000, USA) at 232 nm to optimize the conditions of the microextraction. An amethyst-C18 column (4.6 × 250 mm, 5 μm, Sepax Technologies Inc., USA) was used in all of the experiments. The mobile phase consisted of methanol and water (70:30, v/v), containing 0.4% (v/v) formic acid with a flow rate of 1 mL min⁻¹. Abscisic acid (ABA) and indole-3-acetic acid (IAA) are phytohormones, which may exist in Actinidia chinensis as interferences for the determination of SA. It can be seen from Fig. 3c that the sensitivities for SA in the eluent are generally enhanced with the use of MIMC. The NIMC has an extraction capability that is much lower than that of the MIMC for SA.

The imprinted factor (IF) is defined as follows to assess the selective recognition performance of MIMC:

$$IF = \frac{EF_{MIMC}}{EF_{NIMC}}$$

$$EF = \frac{C_{elu}}{C_0}$$

Here $EF_{MIMC}$ and $EF_{NIMC}$ were the enrichment factors of the analytes extracted in MIMC and NIMC under the same condition, respectively. $C_0$ is the initial concentration of the analyte in the sample solution; $C_{elu}$ is the analyte concentration in eluent. According to the experimental result, the IF is 2.69 for SA, which indicates that MIMC has a higher adsorbability for SA.

Optimization of PMME

In order to obtain a high extraction efficiency, several parameters were optimized (Fig. 4). As can be seen from Fig. 4a, a mixture of PBS (1 × 10⁻³ mol L⁻¹, pH 3.0)-ACN (4:6, v/v) as the desorption solvent displayed a relatively good desorption ability. The added PBS with proper acidity and ionic strength may affect the charge species and the density of the analyte on the sorbent surface, and thus enhances the eluting power of the desorption solvent. In Fig. 4b, 5.0 mL was chosen as the sample solution to obtain both a higher enrichment factor (EF) and recovery of the analyte. In Fig. 4c, the optimized flow rate of the eluent and the sample solution were selected as 0.05 and 0.2 mL min⁻¹, respectively to achieve a high extraction efficiency within a short time. In Fig. 4d, the maximum recovery appeared at an eluent volume of 0.6 mL. However,
to obtain a relatively higher EF and to simplify the following calculation, 0.5 mL was finally chosen as the eluent volume.

**Electrochemical behavior of SA on GO-GCE**

Cyclic voltammetry studies were carried out to determine the electrochemical activity of SA on both bare GCE and GO-GCE in PBS (0.1 mol L\(^{-1}\), pH 7.0). Figure 2c presents the typically crumple and wrinkled structure of GO. Figure 5a shows that there is a clear enhancement of the oxidation peak current for SA on the GO-GCE compared with bare GCE, which indicates that the electrode modified with GO could improve the electrochemical response of SA, due to the increased electroactive surface area as well as the various functional groups of GO that provide active sites for oxidation.\(^{26}\)

Cyclic voltammetry of SA on GO-GCE was implemented at various scan rates. Respective figures are given in Fig. 5b. With scan rates varied from 50 to 300 mV s\(^{-1}\), the oxidation peak potential remains approximately constant at around 1.3 V, the oxidation peak currents (I\(_p\)) increase linearly with the square root of the scan rate, and the calibration equation is 

\[
I_p = 4.3576 \times 10^{-7} \sqrt{v} + 1.4257 \times 10^{-6},
\]

R\(^2\) = 0.9997.  This behavior is typical for a diffusion-kinetic control for the electrode process.

To obtain more information about the oxidation of SA on the GO-GCE, DPV studies were carried out to analyze the dependence of E\(_p\) (peak potential) versus pH. As can be seen from Fig. 5c, E\(_p\) decrease linearly while the pH varies from 1 to 7, and the calibration equation is 

\[
E_p = -0.0360pH + 1.4856,
\]

R\(^2\) = 0.9985.  The negative shift of E\(_p\) indicates that H\(^+\) was involved in the oxidation of SA. According to a reference,\(^{27}\) SA was first transferred the electron to the GO-GCE and lost H\(^+\),

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**Fig. 5**  (A) Cyclic voltammograms of 100 μmol L\(^{-1}\) SA (b, c) on GO-GCE (a, b) and bare GCE (c) in 0.1 mol L\(^{-1}\) PBS (pH 7.0), scan rate: 100 mV s\(^{-1}\).  (B) Cyclic voltammograms of 100 μmol L\(^{-1}\) SA on GO-GCE in 0.1 mol L\(^{-1}\) PBS (pH 7.0) with different scan rates (50 - 300 mV s\(^{-1}\)), inset: the fitting curve between \(\sqrt{v}\) and I\(_p\) of CV.  (C) Differential pulse voltammograms of 100 μmol L\(^{-1}\) SA on GO-GCE in 0.1 mol L\(^{-1}\) PBS with different pH (1 – 7), inset: the fitting curve between pH and E\(_p\) of DPV.

**Fig. 6** DPV peak currents for the oxidation of 10 μmol L\(^{-1}\) SA in 0.1 mol L\(^{-1}\) PBS (pH 7.0) on GO-GCE with different: (a) concentrations of GO; (b) ratio of ACN in PBS.  DPV peak currents for the oxidation of 10 μmol L\(^{-1}\) SA in PBS (include 20% ACN) on GO-GCE (C\(_{GO}\): 2.0 mg mL\(^{-1}\)) with different: (c) pH (C\(_{PBS}\): 0.1 mol L\(^{-1}\)); (d) concentrations of PBS (pH 3.0).
phosphates, which may have hindered the electron transfer, and may be that SA was prone to form hydrogen bonds with the a film with negative charge, \(^{28}\) which would effectively collect around 3.0 due to protonation, while the GO can be regarded as a proportion of SA may exist as the cationic form at a pH of 50 and 60 g g\(^{-1}\); (b) the plots of \(\mu\) reached the maximum at volume ratio of 2:8 (\(V_{ACN}:V_{PBS}\), which allows a better performance compared with at a low concentration. But, excess GO may pile up to increase the electrical resistance of the GCE surface, and thus decrease the current response. In Fig. 6b, the DPV response currents of SA reached the maximum at pH 3.0. Since SA is a diprotic acid in aqueous media with \(pK_a\) value 3.01, a proportion of SA may exist as the cationic form at a pH of around 3.0 due to protonation, while the GO can be regarded as a film with negative charge, \(^{28}\) which would effectively collect cations and reject the diffusion of anions to the film due to the electrostatic interaction. In Fig. 6d, the experimental results present the maximum peak current were obtained at a concentration of 1.0 \(\times\) \(10^{-3}\) mol L\(^{-1}\). A reasonable explanation may be that SA was prone to form hydrogen bonds with the phosphates, which may have hindered the electron transfer, and thus being oxidized to carboxyl-hydroquinone, and further oxidized to carboxyl-para-benzoquinone. Afterwards, carboxyl-para-benzoquinone was reduced to carboxyl-hydroquinone, and diffused into solution.

**SA detection by DPV**

After microextraction by PMME, DPV was employed to detect the extracted SA. The related joint conditions between MIMC and DPV were optimized (Fig. 6). As can be seen from Fig. 6a, with the increase in the concentration of the GO suspension, the DPV response increased. The maximum DPV response could be observed at the electrode modified with 2.0 mg mL\(^{-1}\) of GO. This may be attributed to the high concentration of GO modified on the GCE surface, which allows a better performance compared with at a low concentration. But, excess GO may pile up to increase the electrical resistance of the GCE surface, and thus decrease the current response. In Fig. 6b, the DPV response currents of SA reached the maximum at volume ratio of 2:8 (\(V_{ACN}:V_{PBS}\), which means that the presence of ACN in the measurement system facilitated the electrochemical oxidation of adsorbed SA, rather than interfering with its detection. It could be speculated that ACN increases the solubility of SA, which may affect the density of the analyte on the electrode surface. In Fig. 6c, the peak current of SA reached the maximum at pH 3.0. Since SA is a diprotic acid in aqueous media with \(pK_a\) value 3.01, a proportion of SA may exist as the cationic form at a pH of around 3.0 due to protonation, while the GO can be regarded as a film with negative charge, \(^{28}\) which would effectively collect cations and reject the diffusion of anions to the film due to the electrostatic interaction. In Fig. 6d, the experimental results present the maximum peak current were obtained at a concentration of 1.0 \(\times\) \(10^{-3}\) mol L\(^{-1}\). A reasonable explanation may be that SA was prone to form hydrogen bonds with the phosphates, which may have hindered the electron transfer, and thus lead to a decrease in the peak current. However, the conductivity of the buffer solution would be reduced when the concentration of phosphate was too low.

The stability of GO-GCE was investigated. When not in use, the GO-GCE was stored at 4°C in a refrigerator. The response of GO-GCE to SA lost 4.7% of its original value after storage for 7 days, because the GO was slightly exfoliated from the surface of GCE. The reproducibility of the proposed electrode was tested using five different electrodes. The relative standard deviations (RSD) of the DPV response currents was 6.4% for five different electrodes and 4.1% for the same electrode of five measurements. Thus, the modified electrode displayed high stability and reproducibility.

**Method validation**

The obtained MIMC microextraction was coupled with DPV to establish a method for the determination of SA in *Actinidia chinensis* under the optimized conditions. Figure 7 shows the response of the Actinidia chinensis sample with different spiked concentrations of SA after PMME. Good linearity was obtained in different concentration ranges (Table 1). The limits of detection (LOD, \(S/N = 3\)) and quantification (LOQ, \(S/N = 10\)) were 0.03 and 0.1 \(\mu\)g g\(^{-1}\), respectively. Furthermore, the recoveries of SA in the spiked *Actinidia chinensis* samples were 86.2 – 105.2% (Table 2), which was satisfactory compared with references.\(^{10–13}\) Two kinds of *Actinidia chinensis* samples were selected for the applications of the developed PMME-DPV method. The results showed that the quantities of SA in two *Actinidia chinensis* were 0.056 and 0.077 \(\mu\)g g\(^{-1}\) fresh mass, respectively. As shown in Table 3, a comparison of the proposed method with other methods for determining SA is provided. This demonstrates that the MIMC-PMME-DPV method is comparable to other methods. Thus, the developed method is reliable for the routine analysis of SA in complex *Actinidia chinensis* samples.

### Conclusions

MIMC-PMME followed by DPV was developed as an analytical
Table 3 Comparison of the MIMC-PMME-DPV method with other methods for determining SA

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Method</th>
<th>Linear range/µg L⁻¹</th>
<th>Calibration curve¹</th>
<th>LOD/µg L⁻¹</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>HF-LLLME-HPCL-UV</td>
<td>20–2000</td>
<td>y = 218.48x + 9.95</td>
<td>4.6</td>
<td>Natural coconut juice</td>
<td>10</td>
</tr>
<tr>
<td>SA</td>
<td>SD-LLLME/DART-MS²</td>
<td>4–400</td>
<td>y = 5194x – 5.478</td>
<td>1.1</td>
<td>Fruit juice</td>
<td>11</td>
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<tr>
<td>SA</td>
<td>SPME-LC-UV/DAD</td>
<td>—</td>
<td>—</td>
<td>2.0</td>
<td>Fruits, vegetables, beverages</td>
<td>12</td>
</tr>
<tr>
<td>SA</td>
<td>SBSE-HPLC-UV</td>
<td>10 – 2000</td>
<td>—</td>
<td>0.3 – 2.7</td>
<td>Cucumber, green bean sprouts</td>
<td>13</td>
</tr>
<tr>
<td>SA</td>
<td>Nano-Cu/Au electrode-DPV</td>
<td>—</td>
<td>log I = –5.38 + 0.264 log C</td>
<td>0.1 µmol L⁻¹</td>
<td>Oilseed rape</td>
<td>6</td>
</tr>
<tr>
<td>SA</td>
<td>MIMC-PMMEDPV</td>
<td>0.1–60 µg g⁻¹</td>
<td>y = 0.1609x² + 0.0728</td>
<td>0.03 µg g⁻¹</td>
<td>Actinidia chinensis</td>
<td>This study</td>
</tr>
</tbody>
</table>

References

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Notes

a. y, Peak area; x, concentration of SA (µg L⁻¹). b. HF-LLLME: hollow fiber-based liquid-liquid-liquid microextraction. c. SD-LLLME/DART-MS: single-drop LLLME combined with direct analysis in real-time mass spectrometry. d. SBSE: stir bar sorptive extraction. e. Nano-Cu/Au electrode: copper nanoparticles-modified gold electrode. f. log I: logarithm of the current; log C: logarithm of SA concentration (µmol L⁻¹); g. Y: Current; X: concentration of SA (µg L⁻¹).